

IN THE SPECIFICATION:

On page 1, at line 3, insert the following new paragraph.

- -This is a divisional application of Application No. 09/006,478, filed January 13, 1998, which is a continuation application of Application No. 08/461,975, filed June 5, 1995, now abandoned, which is a divisional of Application No. 08/231,659, filed April 25, 1994, now U.S. Patent No. 5,635,291.- -

Please amend the paragraph starting at page 1, line 4 as follows.

The present invention relates to a recording medium suitable for use in recording using water-based inks, ink jet recording method and a dispersion. In ~~Particular~~ particular, this invention relates to a recording medium which can provide images high in optical density, bright in color tone and high in resolution, and has excellent ink absorbing capacity, an ink-jet recording method using such a recording medium, and a dispersion of an alumina hydrate, which is suitable for use in production of the recording medium.

Please amend the paragraph starting at page 1, line 16, as follows.

In recent years, an ink-jet recording system, in which minute droplets of an ink are flown by any of various working principles to apply them to a recording medium such as paper, thereby conducting recording of images, characters and/or the like, has been quickly spread as a recording apparatus for various images in various applications including information instruments because it has features that recording can be conducted at high speed and with a low noise, color

images can be formed with ease, recording patterns are very flexible, and development and fixing ~~process~~ processes are unnecessary. Further, it begins to be applied to a field of recording of full-color images because images formed by ~~an~~ a multi color ink-jet recording system are comparable in quality with multi-color prints by a plate making system and photoprints by a color photographic system, and such records can be obtained at lower cost than the usual multi-color prints and photoprints when the number of copies is small. With the improvement in recordability, such as speeding up and high definition of recording, and multi-coloring of images, recording apparatus and recording methods have been improved, and recording media have also been required to have higher properties.

Please amend the paragraph starting at page 6, line 11 as follows.

Japanese Patent Application Laid-Open No. 3-281384 discloses an alumina hydrate forming an aggregate like a needle, which is in the form of a column having an aspect ratio of not higher than 3 and unidirectionally oriented, and a process for forming an ink-receiving layer using the alumina hydrate. However, since particles of the alumina hydrate are oriented and compacted, spaces among the alumina hydrate are oriented and compacted, spaces among the alumina hydrate particles in the ink-receiving layer ~~tends~~ tend to narrow. Therefore, the pore radius is partial to a narrow side, and distribution of pore radius has a tendency to narrow. As a result, there is a problem that beading occurs as described above.

Please amend the paragraph starting at page 13, line 25, as follows.

The alumina hydrate can be produced by any conventional method such as the hydrolysis of aluminum alkoxide or sodium aluminate. Rocek, et al. [Collect Czech. Chem. Commun., Vol. 56, 1253-1262 (1991)] have reported that the pore structure of aluminum hydroxide is affected by deposition temperature, pH of the solution, aging time and ~~a kind~~ the kinds of surfactants used.

Please amend the paragraph starting at page 18, line 14 as follows.

The alumina hydrate used in the first aspect of the present invention obtained by the above process is subjected to a hydrothermal synthesis to grow its particles (aging process). The conditions of the aging process can be suitably adjusted to control the pore form of the alumina hydrate particles within a specific range. If the time of the aging is too short, primary particles of the alumina hydrate, which are relatively uneven in particle size, grow, and so the sizes of spaces among the primary particles, which the spaces define pores, become uneven. As a result, it is considered that the range of pore radius distribution widens. The correlation between the degree of unevenness of the primary particles and the range of the pore radius distribution is unclear. The sol obtained may be used as a dispersion as it is as disclosed in Japanese Patent Application Laid-Open No. 2-276670. In the present invention, it is however preferable to dry the sol once into powder by a method such as spray drying and

then prepare a dispersion. In this case, the dispersibility of the alumina hydrate in water is more enhanced.

Please amend the paragraph starting at page 21, line 14, as follows.

Although oxides of magnesium, calcium, strontium, barium, zinc, boron, silicon, germanium, tin, lead, zirconium, indium, phosphorus, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium and the like may be used instead of the titanium dioxide. ~~However, dioxide, however,~~ the titanium dioxide is most preferred from the viewpoint of the adsorptiveness of a dye in an ink and dispersibility. Most of the oxides of the above-mentioned metals are colored, while the titanium dioxide is colorless. From this point, the titanium dioxide is also preferred.

Please amend the paragraph starting at page 24, line 6, as follows.

The alumina hydrate used in the first aspect of the present invention is wide in the half breadth of pore radius distribution, which will be described subsequently, and is dispersed up to a level of primary particles in a dispersion for coating. Such wide pore radius distribution is substantially kept even after the formation of the ink-receiving layer through steps of dispersion of the alumina hydrate, coating on the base material and drying. The reason of for this is not clearly understood. The present inventor however dares to explain for facilitating the

understanding of the present invention, and infers that a pore structure is defined principally by spaces among the primary particles of the alumina hydrate, and the alumina hydrate particles in the form of a flat plate are oriented at random in the ink-receiving layer, or that the wide pore radius distribution attributable to the unevenness of the particle size of the alumina hydrate is kept even in the ink-receiving layer.

Please amend the paragraph starting at page 26-A, line 1, as follows.

The alumina hydrate obtained by the above process is subjected to a hydrothermal synthesis, thereby its particles grow (an aging step). By controlling the conditions of this step, the pore form of the alumina hydrate particles can be controlled within a specified range. Upon setting an aging time suitable, primary particles of the alumina hydrate having relatively even particle size grow, so that the sizes of spaces among the primary particles, which define pores, become even and the range of pore radius distribution becomes narrow. If the aging time is made longer than ~~that~~ these conditions, the alumina hydrate having two tops in the pore radius distribution can be obtained. As a result, a recording medium, in which two tops are made in the pore radius distribution of alumina hydrate, can be obtained. The sol obtained may be used as a dispersion as it is as disclosed in Japanese Patent Application Laid-Open No. 2-276670. In the present invention, it is however preferable to dry the sol once into powder by a method such as

spray drying and then prepare a dispersion. In this case, the dispersibility of the alumina hydrate in water is more enhanced.

Please amend the paragraph starting at page 26-A, line 23, as follows.

The alumina hydrate obtained by the process has two or more peaks in a pore radius distribution. A pore ~~structure is mainly formed by spaces among the primary~~ structure is mainly formed by spaces among the primary particles of the alumina hydrate. The reason why the pore radius distribution has at least two peaks is considered to be as follows. Since the alumina hydrate particles are in the form of a flat plate and the primary particles are oriented at random in the dried powder, there are defined spaces of portions in which primary particles overlap with each other in a direction of the principal ~~plain~~ plane of the flat plate and spaces of ~~another other~~ portions in which an end face and the principal plane or another end face overlap with each other. Thus, two or more peaks in the pore radius distribution are all caused by the spaces among the primary particles, and at least one of the pore radii at one peak becomes smaller than the minor axis or major axis radius of the flat plate surface of the primary particles, while at least one of the pore radii at ~~another other~~ peaks becomes about several times the minor axis or major axis radius of the flat plate surface.

Please amend the paragraph starting at page 26-B, line 20, as follows.

The alumina hydrate of the present invention is, as described above, has at least two peaks in the pore radius distribution. ~~Although~~ Although such ~~the~~ alumina hydrate is dispersed up to a level of primary particles in a dispersion for coating, the radius distribution having at least one ~~peaks~~ peak is kept substantially even when the ink-receiving layer is formed through the steps of dispersing of the alumina hydrate, coating onto a substrate and drying. The reason is considered as follows: Even in an ink-receiving layer, the primary particles of the alumina hydrate are oriented in random direction, as shown by the photograph in Fig. 3, and therefore, as the same as in a case of titanium dioxide-containing alumina hydrate, there are generated spaces of portions in which primary particles overlap with each other in a direction of the principal ~~plain~~ plane of the flat plate through a binder and spaces of ~~another~~ other portions in which an end face and the principal plane or another end ~~face~~ face overlap with each other through a binder, by which the pore radius distribution having two or more peaks is kept even when the ink-receiving layer is formed therefrom.

Please amend the paragraph starting at page 31, line 12, as follows.

In the third aspect of the present invention, the titanium dioxide-containing alumina hydrate is wide in the half breadth of pore radius distribution as described below. Such an alumina hydrate is dispersed up to a level of primary particles in a dispersion for coating. Such wide pore radius distribution is substantially kept even after the formation of the ink-

receiving layer through steps of dispersion of the alumina hydrate, coating on the base material and drying. The reason ~~of~~ for this is not clearly understood, but is considered to be as described above.

Please amend the paragraph starting at page 37, line 3 as follows.

In the recording media according to the first to third ~~aspect~~ aspects of the present invention, which each have an ink-receiving layer on a base material, a relative pressure difference (ΔP) between adsorption and desorption at 90 percent of the maximum amount of adsorbed gas as found from an isothermal nitrogen adsorption and desorption curve for the ink-receiving layer, which is derived from the nitrogen adsorption and desorption method, is preferably not larger than 0.2, more preferably not larger than 0.15, most preferably not larger than 0.10. As described in McBain [J. Am. Chem. Soc., Vol. 57, 699 (1935)], the relative pressure difference (ΔP) can be used as an index whether a pore in the form of an inkpot may exist. The pore is closer to a straight tube as the relative pressure difference (ΔP) is smaller. On the other hand, the pore is closer to an inkpot as the difference is greater. Differences exceeding the above limit result in a recording medium poor in dryness of an ink after printing. Japanese Patent Application Laid-Open No. 60-245588 describes the fact that with respect to the shape of pores in an alumina xerogel used in an ink receiving layer, those low in degree of labyrinth, even and linear are preferred, while an inkpot form narrow in inlet, a gourd form constricted in the

middle and a winding form are not preferred from the viewpoint of rate of absorption. However, this publication does not disclose anything about specific methods for measuring actual physical properties and the like.

Please amend the paragraph starting at page 38, line 19, as follows.

In the recording media according to the first to third ~~aspect~~ aspects of the present invention, the number of hydroxyl groups on the surface of each of the alumina hydrates is preferably at least 10^{20} groups/g. If the number is fewer than this value, the solids concentration of a dispersion in which the alumina hydrate is dispersed in water cannot be increased. Such number of hydroxyl groups on the surface of the alumina hydrate can be determined by the titration with a triethylaluminum solution.

Please amend the paragraph starting at page 39, line 3, as follows.

The surface potential of each of the alumina hydrates used in the present invention can be determined by a zeta potential analyzer. Japanese Patent Application Laid-Open No. 60-232990 discloses that alumina compounds have a positive charge, and in its Examples, the values of zeta-potentials. However, specific measuring ~~method~~ methods and conditions are not described therein. The value of a zeta-potential varies depending upon the cell and electrode structure in a measuring apparatus, applied voltage, the solids concentration and pH of a

dispersion, and dispersants and additives used. Therefore, absolute values cannot be directly compared unless the measuring conditions, apparatus and the like are standardized to conduct the measurement.

Please amend the paragraph starting at page 39, line 17, as follows.

With respect to the alumina hydrates used in the present invention, the zeta-potential is preferably at least 15 mV as measured at pH 6 in the form of a 0.1 % by weight aqueous dispersion free from any dispersant and additive. If the zeta-potential is above this limit, the alumina hydrate can be easily dispersed up to a level of primary particles in a dispersion. If the zeta-potential is lower than 15 mV, aggregate and deposit occur as the solids concentration increases, or particles partly aggregate to form great lumps when a binder dispersion is mixed with the alumina hydrate. For this reason, in particular, in the recording media having an ink-receiving layer, pore radius of the ink-receiving layer becomes markedly large, and so the strength of the ink-receiving layer is lowered, resulting in a potential problem that dusting may occur, or dye-fixing ability upon printing may be deteriorated. In general, alumina hydrate is stable in a low pH region. It is therefore known to add an acid to ~~low~~ lower the pH of the dispersion. However, the addition of the acid is not preferred from the viewpoint of the occurrence of offensive odor and corrosion and of the limitation of the kind of binder used.

Further, a known process in which a dispersant is added is not preferred because repellent or the like occurs upon the coating of the dispersion.

Please amend the paragraph starting at page 41, line 7, as follows.

In the present invention, a dispersion obtained by dispersing an alumina hydrate containing 0.1 to 1.0 % by weight of a nitrate anion, said alumina hydrate being such a specific alumina hydrate as described above, in deionized water to give a solids concentration of 15 % by weight preferably has a viscosity of not higher than 75 cP, most preferably not higher than 30 cP as measured at 20 °C and a shear rate of 7.9 sec⁻¹. Further, a dispersion obtained by dispersing the same alumina hydrate containing 0.1 to 1.0 % by weight of a nitrate anion as described above in deionized water to give a solids concentration of 20 % by weight preferably has a viscosity of not higher than 100 cP, most preferably not higher than 80 cP as measured at 20°C and a shear rate of 10.2 sec⁻¹. Furthermore, a dispersion obtained by dispersing the same alumina hydrate containing 0.1 to 1.0 % by weight of a nitrate anion as described above in deionized water to give a solids concentration of 25 % by weight preferably has a viscosity of not higher than 500 cP, most preferably not higher than 460 cP as measured at 20°C and a shear rate of 10.2 sec⁻¹. In each of the above cases, if the viscosity exceeds the upper limit, the dispersion is required to ~~low~~ lower its solids concentration. It is not hence preferable from the viewpoint of mass productivity to increase the viscosity beyond the above limit.

Please amend the paragraph starting at page 46, line 16, as follows.

The prior art describes a psuedoboehmite sol and a production process of an ink-receiving layer making use of the sol. On the contrary, the non-crystal titanium dioxide-containing alumina ~~hydrates~~ hydrate in the form of a flat plate according to the present invention is produced by hydrolyzing, preferably, an aluminum long-chain alkoxide and titanium alkoxide. Therefore, it is possible to obtain an alumina hydrate containing little ion and raw alcohol with ease. According to this process, the alumina hydrate ~~tend~~ tends to become particles in the form of a flat plate, and shape control can be made with ease. Further, titanium dioxide exists in the close vicinity of the surfaces of the particles, so that the alumina hydrate has far higher dispersibility than the known alumina hydrate in the needle form. Furthermore, the resulting titanium dioxide-containing alumina hydrate is dried once to powder without directly preparing a dispersion (in particular, a dispersion for coating) in a sol state, and then used, whereby a dispersion high in solids concentration and low in viscosity can be prepared with ease.

Please amend the paragraph starting at page 47, line 10, as follows.

In each of the recording media according to the present invention, a binder capable of ~~using~~ being used in combination with the alumina hydrate may be freely selected from water-soluble polymers. For example, preference may be given to polyvinyl alcohol or modified

products thereof (cationically modified, anionically modified, silanol modified), starch or modified products thereof (oxidized, etherified), casein or modified products thereof, gum arabic, cellulose derivatives such as carboxymethyl cellulose, hydroxyethyl cellulose and

- hydroxypropylmethyl cellulose, conjugated diene copolymer latexes such as SBR latexes, NBR latexes and methyl methacrylate-butadiene copolymers, functional group modified polymer latexes, vinyl copolymer latexes such as ethylene-vinyl acetate copolymers, polyvinyl pyrrolidone, maleic anhydride polymer or copolymers thereof, acrylic ester copolymers, and the like. These binders may be used either singly or in any combination thereof. The mixing ratio of the alumina hydrate to the binder may be optionally selected from a range of from 1:1 to 30:1, preferably from 5:1 to 25:1. If the amount of the binder is less than the lower limit of the above range, the mechanical strength of the resulting ink-receiving layer is insufficient, which forms the cause of cracking and dusting. If the amount is greater than the upper limit of the above range, the pore volume of the resulting ink receiving layer is reduced, resulting in a recording medium poor in ink absorptiveness.

Please amend the paragraph starting at page 49, line 22, as follows.

In the recording media having an ink-receiving layer according to the present invention, as a process for forming the ink-receiving layer on the base material, may be used a process in which the dispersion containing the alumina hydrate and the like is applied to the base

material by means of a coater, and then dried. As a coating process, may be used a generally-used coating technique making use of a blade coater, air knife coater, roll coater, brush coater, curtain coater, bar coater, gravure coater or sprayer. The coating weight of the dispersion is - within a range of from 0.5 to 60 g/m², more preferably from 5 to 45 g/m² in dried state. As - needed, the resulting recording medium may by be subjected to supercalendering or the like so as to improve the smoothness of the ink-receiving layer.

Please amend the paragraph starting at page 49, line 24, as follows.

Inks used in conducting recording on the recording media according to the present invention ~~comprises~~ comprise principally a coloring material (dye or pigment), a water-soluble organic solvent and water. Preferred examples of the coloring material include water-soluble dyes represented by direct dyes, acid dyes, basic dyes, reactive dyes and food colors. However, any coloring materials may be used so far as they provide images satisfying required performance such as fixing ability, coloring ability, brightness, stability, light fastness and the like in combination with the above-described recording media.

Please amend the paragraph starting at page 52, line 19, as follows.

A solubilizer may be added to the inks. Nitrogen-containing heterocyclic ketones are typical solubilizers. Its object is to enhance the solubility of the water soluble dye in the

solvent by leaps and bounds. For example, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone are preferably used. In order to further improve the properties of inks, there may be added additives such as viscosity modifiers, surfactants, surface tension modifiers, pH adjustors and specific resistance adjustors.

Please amend the paragraph starting at page 55, line 24, as follows.

The content of titanium dioxide in the whole alumina hydrate sample was determined by fusing the alumina hydrate sample in a borate in accordance with the ICP method (SPS 4000, manufactured by Seiko-Electronic Inc.). The distribution of titanium dioxide in the alumina hydrate sample was analyzed by means of an ESCA (Model 2803, manufactured by Surface Science Instruments Co.). The surface of the alumina hydrate sample was etched with an argon ion for 100 seconds and 500 seconds to determine the change in content of the titanium dioxide. Etching conditions ~~was~~ were as follows:

Please amend the paragraph starting at page 57, line 7, as follows.

Polyvinyl alcohol (Gohsenol NH18, product of The Nippon Synthetic Chemical Industry Co., Ltd.) was dissolved or dispersed in deionized water to obtain a 10 % by weight solution or dispersion. The four different kinds of alumina hydrates obtained above were separately similarly dispersed in deionized water to obtain 15 % by weight dispersions. Each of

the alumina hydrate dispersions and the polyvinyl alcohol solution were weighed out to give a weight ratio of 10:1 in terms of solids and mixed with each other. The resultant mixture was stirred to obtain a mixed dispersion. The mixed dispersion was applied by a die coating process to one side of a PET film (Lumirror, product of Toray Industries, Inc.) having a thickness of 100 μm to form an ink receiving ~~layers~~ layer having a thickness of 30 μm . Fig. 4 is a photograph (an electron microphotograph: 50,000 magnifications) illustrating the section of the ink receiving layer and indicates that the alumina hydrate in the form of a flat plate lies at random in the ink receiving layer. The physical property values of the ink receiving layer were measured in accordance with the respective methods described above. The results are shown in Table 3. Printing was conducted on the thus-obtained recording media to evaluate their printability in accordance with the following standards. The evaluation results are also shown in Table 3.

Please amend the paragraph starting at page 61, line 3, as follows.

A paper web having a basis weight of 70 g/m² was made by means of a TAPPI standard sheet ~~former~~ formed by using, as raw pulp, 80 parts of bleached hardwood kraft pulp (LBKP) having a freeness (C.S.F.) of 370 ml and 20 parts of bleached softwood kraft pulp (NBKP) having a freeness of 410 ml, incorporating, as a filler, each of the alumina hydrates prepared in Examples 1 to 4 in a proportion of 35 % by weight based on the solid content of the pulp and as a retention aid, cationic starch (CATOF, product of Oji National K.K.) in a proportion

of 0.3 % by weight based on the solid content of the pulp into the pulp, and the adding 0.05 % by weight of a polyacrylamide retention aid (Pearlflock FR-X, product of Seiko Chemical Industries Co., Ltd.) right before paper making. A 2 % solution of oxidized starch (MS3800, product of Nihon Shokuhin Kako Co., Ltd.) was then applied to the web by a size press to obtain a recording ~~media~~ medium. Printing was conducted on the thus-obtained recording media to evaluate their printability in accordance with the above-described standards. The evaluation results are shown in Table 5.

Please amend the paragraph starting at page 85, line 4, as follows.

While the present invention has been described with respect to what is presently considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, the invention is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims. The scope of the following claims is to be accorded to the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.